Australian Journal of Basic and Applied Sciences, 5(11): 2230-2236, 2011
ISSN 1991-8178

Using fuzzy interpolation for studying removal of Tartrazin by UV/TiO_2 process

[1]F Ghanbary, [2]A Jafarian, [3]N Modirshala, [3]M.A. Behnajady, [4]M Khosravi

[1]Department of Applied Chemistry, Faculty of Chemistry, Mahabad Branch, Islamic Azad university, Mahabad, Islamic Republic of Iran.
[2]Department of Mathematics, Faculty of Mathematics, Ourmia Branch, Islamic Azad university, Ourmia, Islamic Republic of Iran.
[3]Research Laboratory, Department of Applied Chemistry, Tabriz Branch, Islamic Azad university, P.O. box 1655, Tabriz, Islamic Republic of Iran.
[4]Department of Applied Chemistry, Faculty of Chemistry, North Tehran Branch, Islamic Azad university, Tehran, Islamic Republic of Iran.

Abstract: The removal of tartrazin by UV/TiO_2 process was investigated. The effect of parameters such as initial concentration of dye, UV light intensity, initial dosage of nano TiO_2 and time were investigated. The results were not exactly the same by repeating the tests in the same conditions, so we use fuzzy logic to show the vagueness and uncertainty. In fact by using fuzzy set theory and fuzzy interpolation, mathematical method was presented for removal of the Tartrazin by UV/TiO_2 process.

Key words: Fuzzy interpolation, Tartrazin, Removal, UV/TiO_2 process.

INTRODUCTION

Synthetic dyes are the major industrial pollutants and water contaminants (Brown *et al*., 1981; Vaidya and Datye, 1982; Modirshahla *et al*., 2007; Behnajady *et al*., 2007). Textile wastewater introduces intensive color and toxicity to aquatic systems which is mostly non-biodegradable and resistant to destruction by physicochemical treatment methods (Daneshvar *et al*., 2005).

One of the most active areas in environmental research is the development of highly efficient methods for the elimination of hazardous pollutants from air, soil and water (Castro *et al*., 2008). Recently, chemical treatment methods, based on the generation of hydroxyl radicals, known as advanced oxidation processes (AOPs) have been developed (Behnajady *et al*., 2007). AOPs have attracted wide interests in wastewater treatment since the 1990s (Modirshahla *et al*., 2007).

The development of UV/TiO_2 process in order to achieve complete mineralization of organic pollutants has been widely tested for a large variety of industrial dyes (Behnajady *et al*., 2007; Ghanbary *et al*., 2011). Semiconductors used for such applications should have a high resistance to photocorrosion, water hydrolysis processes and low cost. Their photosensitivity should be efficient when using the solar spectrum and have a high quantum efficiency.

From mathematical point of view, most measurements can be assumed to be fuzzy values because absolute precision of such measurements cannot be guaranteed. There are some statistical tests, which are sensitive to the appearance of rough abnormities in spatial time series (Waelder, 2007; Waelder, 2005; Waelder, 2004). Another point of view uses the fact that interpolation data are not sets of real numbers but are ranges of values. The distribution within the range may not necessarily be probabilistic. The difference between error and uncertainty is explained by Lodwick (Lodwick and Santos, 2003): Error assumes that a true value exists. Uncertainty denotes incomplete knowledge that is characterized by whether or not one can say that a proposition is exclusively true or false. A statement is uncertain when its (exclusive) true or falseness can be ascertained.

Uncertainty can be modeled using some useful approaches, which are developed in the fuzzy set theory. The so-called interval arithmetic belongs to these approaches. A measurement is considered to be a mathematical object, an interval with two fixed borders: (real) under and upper limit values, see Fig. 1. The assumed measurement uncertainty can be modelled using the variable width of this interval. It should be noted that an interval is the simplest fuzzy object. A helpful introduction to fuzzy theory has been reported by Bandemer (Bandemer and Gottwald, 1993). Some useful definitions related to fuzzy arithmetic has been described by Anile (Anile *et al*., 2000).

A fuzzy value describes incomplete knowledge about a value. Fuzzy values can be modeled by convex fuzzy sets. Their characterizing function should have exactly one local maximum (Waelder, 2007). The support of triangular fuzzy numbers corresponds to an interval with fixed borders, see Fig. 1. The fuzzy interval calculation uses and generalizes methods of the interval arithmetic. These methods are also applied in the so-called adjustment theory in geodesy (Wolf, 1997). Corresponding to the point of view appearing in fuzzy theory, one handles with intervals, whose variable width reflect a measure of the uncertainty instead of variances of

Corresponding Author: Ghanbary, Department of Applied Chemistry, Faculty of Chemistry, Mahabad Branch, Islamic Azad university, Mahabad, Islamic Republic of Iran.
E-mail: Ghanbary83@yahoo.com

random values in probabilistic approaches. More details about interval arithmetic has been described by Alefeld (Waelder, 2007).

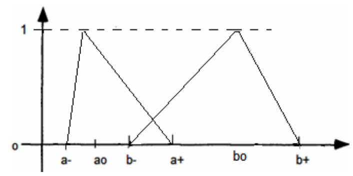

Fig. 1: A schematic presentation of two fuzzy intervals A=[a-, ao, a+] and B=[b-, bo, b+] with their characterizing functions.

Recently, fuzzy set theory has been used to utilize imprecise information in a non-probabilistic sense and to allow use of information of different quality in the modeling and evaluation process. Fuzzy sets describing imprecision or vagueness were first introduced by Zadeh (Schulz *et al*., 1999) and have been applied in different fields such as decision making and control (Dubois and Prade, 1980), geostatistics and geophysics (Schulz *et al*., 1999).

The results were different by repeating the tests in the same conditions, so we use fuzzy logic to show the vagueness and uncertainty. In fact by using fuzzy set theory and fuzzy interpolation, mathematical method was presented for removal of the Tartrazin by UV/TiO_2 process.

MATERIALS AND METHODS

Materials:

Nano TiO_2 was prepared in the previous work (Ghanbary *et al*, 2011). Tartrazin was obtained from Merck (Germany) and used without any further purifications. Deionized water was used throughout the work.

Ultrasonic Bath (T 460/H):

The ultrasonic bath Elma (GmbH) was used with the operating frequency of 35 kHz and a rated output power of 170 W. The bath has the dimensions of 240 mm×137 mm×100 mm. The total internal body is made from stainless steel.

Method:

In order to get nanostructured TiO_2, $Ti(OC_3H_7)_4$ solution was dissolved in MeOH and the mixture was sonicated for 3 min and agitated at 70°C for 210 min under magnetic stirrer. Water was added dropwise into the hot solution (70°C) during this period of time. The precipitate was isolated by filtration, washed with hot water and organic solvents to remove the adsorbed impurities and calcined at 400 °C for 3 h (Ghanbary *et al*, 2011).

All photocatalytic experiments were carried out in a batch photoreactor. The radiation source was a low pressure mercury UV lamp (30 W, UV-C, λ_{max} = 254 nm, manufactured by Philips, Holland), which was placed above a batch photoreactor of 0.5 L volume. The incident UV light intensity was measured by a Lux-UV-IR meter (Leybold Co.). In each experiment, a known amount of TiO_2 was added to 500 ml of the solution and a magnetic stirrer was used in order to achieve a homogeneous mixture.

Analytical Method:

In the presence of TiO_2 as photocatalyst, Tartrazin was used as pollutant. Sample solutions were sonicated before irradiation for 5 min. At known irradiation time intervals, the samples (5 ml) were taken out and then analyzed by UV-Vis spectrophotometer (Ultrospec 2000, Biotech Pharmacia, England) at 428 nm. A linear correlation was established between the Tartrazin concentration and the absorbance, in the range 0–60 mg/L with a correlation coefficient, R^2=0.9991. The equation used to calculate the photocatalytic removal efficiency (R) in the experiments was:

$$R(\%) = \left(\frac{C_0 - C}{C_0}\right) \times 100 \quad (1)$$

Where C_0 is the initial concentration of the Tartrazin (mg/L) and C is the concentration of the Tartrazin (mg/L) at time t.

Fuzzy Software:

All Fuzzy calculations were carried out using Matlab 7.8 (2009R) mathematical software with *** toolbox. We have used triangular membership function for design of fuzzy model. Fuzzy Lagrange polynomial was used for interpolation of fuzzy data.

RESULTS AND DISCUSSION

Photocatalytic Studies:

In order to examine the photocatalytic activity of the prepared samples, the photocatalytical removal of Tartrazin in presence of nonopowder was studied.

Fuzzy Sets and Fuzzy Logic:

Fuzzy sets were introduced by Zadeh (Zadeh, 1965) as a means of representing and manipulating data that was not precise, but rather fuzzy. There is a strong relationship between Boolean logic and the concept of a subset, there is a similar strong relationship between fuzzy logic and fuzzy subset theory. In classical set theory, a subset A of a set X can be defined by its characteristic function X_A as a mapping from the elements of X to the elements of the set {0, l}, $X_A: X \rightarrow \{0, 1\}$.

This mapping may be represented as a set of ordered pairs, with exactly one ordered pair present for each element of X. The first clement of the ordered pair is an element of the set X and the second clement is an element of the set {0, l}. The value zero is used to represent non-membership and the value one is used to represent membership. The truth or falsity of the statement "x is in A" is determined by the ordered pair (x, X_A(x)). The statement is true if the second element of the ordered pair is 1 and the statement is false if it is 0.
Similarly, a fuzzy subset A of a set X can be defined as a set of ordered pairs, each with the first element from X and the second element from the interval [0, 1], with exactly one ordered pair present for each element of X. This defines a mapping, μ_A, between elements of the set X and values in the interval [0, 1]. The value zero is used to represent complete non-membership, the value one is used to represent complete membership and values in between are used to represent intermediate degrees of membership. The set X is referred to as the universe of discourse for the fuzzy subset A. Frequently, the mapping μ_A is described as a function, the membership function of A. The degree to which the statement "x is in A" is true is determined by finding the ordered pair (x,μ_A(x)). The degree of truth of the statement is the second element of the ordered pair. It should be noted that the terms membership function and fuzzy subset get used interchangeably. In the other hand a fuzzy set, A in X is characterized by its membership function.

$$\mu_A: X \rightarrow [0, 1]$$

And μ_A(x) is interpreted as the degree of membership of element x in fuzzy set A for each x ∈X.
It is clear that A is completely determined by the set of tuples

$$A = \{x, \mu_A(x)) \mid x \in X\}$$

A fuzzy set A is called triangular fuzzy number with peak (or center) a, left width α > 0 and right width **β** > 0 if its membership function has the Following form

$$A(t) = \begin{cases} 1 - \dfrac{a-t}{\alpha} & if\ a - \alpha \le t \le a \\ 1 - \dfrac{t-a}{\beta} & if\ a \le t \le a + \beta \\ 0 & otherwise \end{cases}$$

And we use the notation A = (a, α, β).

It can easily be verified that $[A]^\gamma = [a - (1-\gamma)\alpha, (1-\gamma)\beta], \ \forall \gamma \in [0,1]$
The support of A is (a - α, a + β).

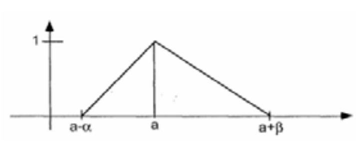

Fig. 2: Triangular fuzzy number Suppose we want to define the set of natural numbers "close to 1 ". This can be expressed. By A= 0.0/ - 2 + 0.3/ - 1 + 0.6/0 + 1.0/1 + 0.6/2 + 0.3/3 + 0.0/4.

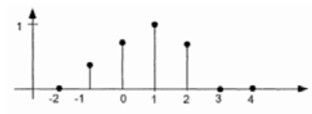

Fig. 3: A discrete membership function for x is close to 1.

Membership functions are constructed taking into account the context of interest. The most commonly adopted shapes for the diagram of the membership functions are triangular or trapezoidal: e.g. if we consider the set of the ' real numbers that are close to 3', a reasonable interval is $1 \le x \le 5$. Then the diagrams will be symmetrical, with $\mu = 0$ in correspondence to x=1 and x=5 (because 1 and 5 are the points with minimum correspondence to the property considered, within the selected interval) and $\mu = 1$ in correspondence to x=3 (because the closest value to 3 is 3 itself). A triangular shape of the diagram will correspond to a linear decrease of the value of the membership function as the 'distance' from 3 of the real number considered increases on either . Other criteria for the assignation of the values of the membership function can be selected, assigning higher importance to the real numbers that are closer to 3; then different diagrams are obtained in correspondence to the different criteria (Mammino, 2004).

Fuzzy Interpolation:

Suppose we have n + 1 points $x_0 < x_1 < \dots < x_n$ in R. To each x_i we associate a fuzzy number $u_i \in \mathcal{F}$ Our purpose is to study continuous functions f: $\mathbb{R} \to \mathcal{F}$ such that $f(x_i) = u_i$ for all i = 0 ,. . . , n. Lowen (Lowen, 1990) gave a fuzzy interpolation polynomial of Lagrange type and proved that it is continuous with respect to the metric H, where H(u, v) is the Hausdorff metric between endographs of u and v, cf (Kaleva, 1994).

The interpolation polynomial p of Lowen can be written levelwise as follows. If $p^{\propto}(x)$ is the $\propto$-level set of p(x) then.

$$p^{\propto}(x) = \{y \in \mathbb{R} | y = p_{d_0 \dots d_n}(x), d_i \in u_i^{\propto}\} \tag{2}$$

Where $p_{d_0 \dots d_n}$, is the Lagrange interpolation polynomial interpolating the data (x_i, d_i), i = 0 , . . . , n. In the next section we give a form, which is more convenient for computation.

The Fuzzy Lagrange Polynomial:

Let

$$L_i(x) = \prod_{\substack{j=0 \\ j \neq i}}^{n} \frac{(x - x_i)}{(x_i - x_j)}. \tag{3}$$

Then $p_{d_0 \dots d_n}(x) = \sum_{i=0}^{n} d_i L_i(x)$ and by definition

$$p^{\propto}(x) = \sum_{i=0}^{n} L_i(x) u_i^{\propto}. \tag{4}$$

Hence

$$p(x) = \sum_{i=0}^{n} L_i(x) u_i \tag{5}$$

The function p is continuous and if $x \in (x_i, X_{i+1})$ then for all $\propto \in [0, 1]$

$$len\, p^{\propto}(x) \ge min\{len p^{\propto}(x_i), len\, p^{\propto}(x_{i+1})\}, \tag{6}$$

Where len denotes the length of an interval.

The continuity follows immediately from (5). Since the addition does not decrease the length of an interval we have

$$len\, p^{\propto}(x) \ge len\left(\sum_{j=i}^{i+1} L_j(x) u_j^{\propto}\right) \ge min\{len\, u_i^{\propto}, len\, u_{i+1}^{\propto}\} \sum_{j=i}^{i+1} |L_j(x)|. \tag{7}$$

Furthermore, since $L_i(x) + L_{i+1}(X) \ge 1$ for all $x \in (x_i, X_{i+1})$ we have the theorem.

The last claim is seen as follows. The polynomial $L_i(x) + L_{i+1}(x)$ is of degree n and interpolates the data (x_j, f_j), where f_j=1 for j=i, i+l and zero otherwise. Suppose that 0<i<n-1 and

$L_i(x) + L_{i+1}(x) < 1$ for some $x \in (x_i, x_{i+1})$. Then its derivative has at least three zeros on (x_{i-1}, x_{i+1}). By the mean value theorem the derivative has a zero on (x_j, X_{j+l}), for $0 \leq j \leq i - 2$, $i + 2 \leq j \leq n - 1$. Then it has at least n zeros, which is a contradiction. The cases i = 0 and i = n - 1 are treated similarly.

Denote $u_i^{\propto} = [a_i^{\propto}, b_i^{\propto}]$. Then the upper end point of $p^{\propto}(x)$ is the solution of the optimization problem maximize $p_{d_0 \dots d_n}(x)$

subject to $a_i^{\propto} \leq d_i \leq b_i^{\propto}$, i = 0 , . . . , n .

It follows that the optimal solution is

$$d_i = \begin{cases} b_i^{\propto} \; if \; L_i(x) \geq 0, \\ a_i^{\propto} \; if \; L_i(x) < 0, \end{cases} \tag{8}$$

Since for all $x \in (x_j, x_{j+1})$

$$Sign \; L_i(x) = \begin{cases} (-1)^{i-j-1} \; for \; 0 \leq j \leq i - 1, \\ (-1)^{j-i} \; for \; i \leq j \leq n - 1 \;, \end{cases} \tag{9}$$

We can easily find the optimum value for d_i, form the corresponding interpolation polynomial and hence obtain the upper end point of $p^{\propto}(x)$ on the whole interval (x_j, X_{j+l}).

Similarly the lower end point on (x_j, x_{j+1}) is obtained as the value of the interpolation polynomial associated to points

$$d_i = \begin{cases} b_i^{\propto} \; if \; L_i(x) < 0, \\ a_i^{\propto} \; if \; L_i(x) \geq 0, \end{cases} \tag{10}$$

From (5) it directly follows that if u_i is an L-L fuzzy number, cf. (Dubois and Prade, 1980) for all i then also p(x) is such a fuzzy number for each x. More precisely, if $u_i = (m_i, l_i, r_i)$ then p(x) = (re(x), l(x),

r(x)), where

$$m(x) = \sum_{i=0}^{n} L_i(x) m_i, \tag{11}$$

$$l(x) = \sum_{L_i(x) \geq 0} L_i(x) l_i - \sum_{L_i(x) < 0} L_i\,(x) r_i \tag{12}$$

$$r(x) = \sum_{L_i(x) \geq 0} L_i(x) r_i - \sum_{L_i(x) < 0} L_i\,(x) l_i \tag{13}$$

Note that the triangular fuzzy numbers are special cases of L-L fuzzy numbers.

Since the interpolation polynomial may wiggle between the data points, the same is true for the fuzzy interpolation polynomial. In the next section we introduce a fuzzy spline for diminishing the wiggling.

Effect of Nano Tio$_2$ Dosage:

The photocatalytic removal of Tartrazin in aqueous solution with various nano TiO_2 dosage was studied. The results were not exactly the same by repeating the tests in the same conditions, so we use fuzzy logic to show the vagueness and uncertainty. The fuzzy data plot was shown in Fig. 4. Apparently, in this work, the photodegradation efficiency of Tartrazin increased when the concentration of TiO_2 increased. This was mainly because of the increase of hydroxyl radical produced from irradiated TiO_2. When we increased the dose of the catalyst, of course, it would increase the adsorption amount of the reaction target resulting in a faster degradation rate. However, high dosage of TiO_2 particles became much easier to aggregate and reduced the light transmission.

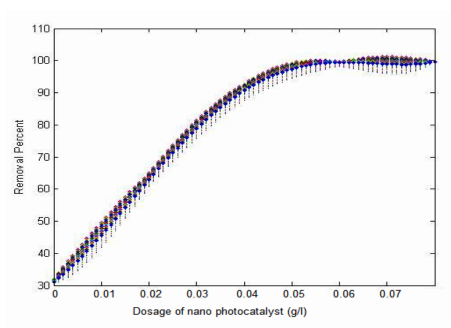

Fig. 4: Removal percent of Tartrazin in the presence different dosage of TiO_2 nanophotocatalysts $[Tartrazin]_0$= 40 mg/L, UV=30.3 W/m^2, Time=50 min.

Effect of Irradiation Time:

Reaction time influences the treatment efficiency of the UV/TiO_2 process. Fig. 5 shows the relationship between the removal efficiency and the photocatalytic reaction time. Because of different results in same condition, the data was shown in fuzzy plot.

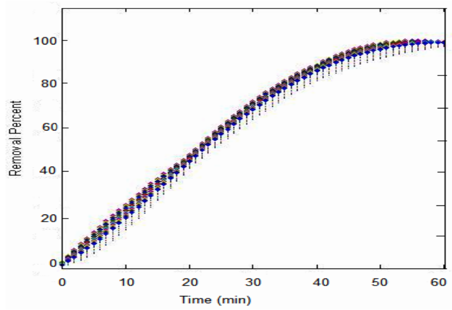

Fig. 5: Effect of time on the removal percent of Tartrazin [Nano TiO_2]$_0$= 0.03 g/L, [Tartrazin]$_0$= 40 mg/L, UV=30.3 W/m^2.

Effect of UV Light Intensity:

The Tartrazin removal efficiency during the reaction period under different UV light intensity has been presented in Fig. 6. The figure clearly shows that the removal rate increases by increasing UV irradiation intensity. Also this fig. shows that the results are uncertain in same condition therefore the fuzzy data has been used for drawing the plot.

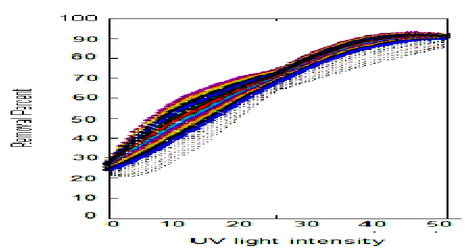

Fig. 6: Effect of UV light intensity on the removal percent of Tartrazin [Tartrazin]$_0$= 0.03 g/L, [4-NP]$_0$= 20 mg/L, Time=50 min.

Effect of 4-NP Initial Concentration:

It is important from an application point of view to study the dependence of removal efficiency on the initial concentration of the Tartrazin. Therefore, the effect of Tartrazin concentration on the removal efficiency was investigated. The fuzzy removal percent was plotted versus initial Tartrazin concentration in Fig. 7.

When the Tartrazin concentration increases, the amount of Tartrazin molecules adsorbed on the surface of the catalyst increases. This affects the photocatalytic activity of TiO_2 and reduce the photocatalytic efficiency. The increase in the Tartrazin concentration also decreases the path of photons into the Tartrazin solution. At high concentration, the Tartrazin molecules may absorb a significant amount of light and this may also reduce the photocatalytic efficiency (Chakrabarti and Dutta, 2004).

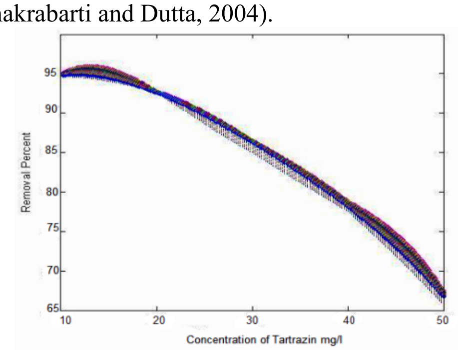

Fig. 7: Effect of initial concentration of Tartrazin on the removal percent [Nano TiO_2]$_0$= 0.03 g/L, UV=30.3 W/m^2, Time=50 min.

Conclusion:

The results showed that UV/TiO_2 process is powerful method for decolorization of Tartrazin. The mathematical model was presented for removal of the Tartrazin with UV/TiO_2 process by using fuzzy set theory and fuzzy interpolation. In fact we applied fuzzy logic to show the vagueness and uncertainty of the experimental data.

ACKNOWLEDGEMENT

The authors would like to thank Islamic Azad University of Mahabad branch for financial supports.

REFERENCES

Anile, A.M., B. Falcidieno, G. Gallo, M. Spagnuolo, S. Spinello, 2000. Modeling uncertain data with fuzzy B-splines, Fuzzy Sets and Systems, 113: 397-410.

Behnajady, M A., N. Modirshahla, N. Daneshvar, M. Rabbani, 2007. Photocatalytic degradation of an azo dye in a tubular continuous-flow photoreactor with immobilized TiO_2 on glass plates. Journal of Chemical Engineering, 127: 167-176.

Behnajady, M.A., N. Modirshahla, F. Ghanbary, 2007. A kinetic model for the decolorization of C.I. Acid Yellow 23 by Fenton process. Journal of Hazardous Materials, 148: 98-102.

Brown, D.H., H.R. Hitz, L. Schafer, 1981. The assessment of the possible inhibitory effect of dye stuffs on aerobic wastewater: experience with a screening test. Chemosphere, 10: 245-261.

Castro, A.L., M.R. Nunes, A.P. Carvalho, F.M. Costa, M.H. Florencio, 2008. Synthesis of anatase TiO_2 nanoparticles with high temperature, stability and photocatalytic activity. *Solid State Sciences,* 10: 602-606.

Chakrabarti, S., B.K. Dutta, 2004. Photocatalytic degradation of model textile dyes in wastewater using ZnO as semiconductor catalyst. Journal of Hazardous Materials, 112: 269-278.

Daneshvar, N., M. Rabbani, N. Modirshahla, M.A. Behnajady, 2005. Photooxidative degradation of Acid Red 27 in a tubular continuous-flow photoreactor : influence of operational parameters and mineralization products. Journal of Hazardous Materials, 118: 155-160.

Dubois, D., H. Praed, 1982, Towards fuzzy differential calculus: Part 3, differentiation. Fuzzy Sets and Systems, 8: 225-233.

Ghanbary, F., N. Modirshahla, M. Khosravi, M.A. Behnajady, 2011. Synthesis of TiO_2 nanoparticles in different thermal conditions and modeling its photocatalytic activity with artificial neural network. Journal of Environmental Sciences, Article in press.

Kandel, A., 1994. Interpolation of fuzzy data. Fuzzy Sets and Systems, 61: 63-70.

Lodwick, W.A., J. Santos, 2003. Constructing consistent fuzzy surfaces from fuzzy data. Fuzzy Sets and Systems, 135: 259-277.

Mammino, L., 2004. Mentioning fuzzy logic in theoretical chemistry courses: motivations and extent. Journal of Molecular Structure (Theochem), 709: 231-238.

Modirshahla, N., M.A. Behnajady, F. Ghanbary, 2007. Decolorization and mineralization of C.I. Acid Yellow 23 by Fenton and photo-Fenton processes. Dyes and Pigments, 73: 305-310.

Schulz, K., B. Huwe, S. Peiffer, 1999. Parameter uncertainty in chemical equilibrium calculations using fuzzy set theory. Journal of Hydrology, 217: 119-134.

Vaidya, A.A., K.V. Datye, 1982. Environmental pollution during chemical processing of synthetic fibres. Colourage , 14: 3-10.

Waelder, O., 2005. Ein empirisches statistisches Verfahren zur Indikation der Detenabnormitaten mittels spezieller wavelet-splines, Journal of Austrian Statist., 34(3): 251-261.

Waelder, O., 2007. An application of the fuzzy theory in surface interpolation and surface deformation analysis. Fuzzy Sets and Systems, 158: 1535-1545.

Waelder, O., M. Buchroithner, 2004. A method for sequential thinning of digital raster terrain models, Journal of Photogrammetry Remote Sensing Geoinform, 3: 215-221.

Wolf, H., 1997. Ausgleichungsrechnung, Ferd. Duemmlers Verlag, Bonn. Zadeh L.A., 1965. Fzzy sets. Information Control, 8: 338-353.